VI.3 A High Temperature (400 to 650°C) Secondary Storage Battery Based on Liquid Sodium and Potassium Anodes

Objectives

- Develop an energy storage device based on an alkali metal ion conducting beta" alumina solid electrolyte (BASE) (high temperature battery).
- Investigate materials for suitable electrochemical couples.
- Fabricate both tubular and planar BASE possessing high strength, high conductivity, and high moisture-resistance.
- Design and construct an optimized planar battery.
- Evaluate the charge-discharge capability of batteries at elevated temperatures.

Accomplishments

- Fabricated Na-BASE tubes by MSRI's patented vapor phase process.
- Constructing a battery tester with controlled temperature and atmosphere.
- Identification of suitable materials for electrochemical couples.

Introduction

A solid oxide fuel cell (SOFC) is an energy conversion device, which efficiently converts the chemical energy in hydrocarbon fuels directly into electricity at a high efficiency without the need for moving parts, except those for auxiliary pumps and blowers. As an electricity generator, its most efficient, practical and realistic use is in combination with an efficient energy storage device for electric-power generation and distribution application, particularly for utility load leveling and peak shaving. However, the associated energy storage devices of the integrated energy conversion-storage system must be capable of a very high roundtrip efficiency. Suitable batteries and reversible SOFC (solid oxide electrolysis cell – SOEC) could be the candidates serving as the energy storage devices in different energy forms, which are electrical energy and chemical energy carried by hydrogen. Due to the inherent limitations, such as hydrogen gas storage and parasitical losses, the SOEC doesn't have enough high roundtrip efficiency. Instead, load leveling batteries, which have been under development widely outside of the U.S., are capable of achieving a high roundtrip efficiency. An advanced high-temperature energy storage battery, based on an alkali metal ion conducting beta" alumina solid electrolyte (BASE) and a non-corrosive metal salt, is proposed and will be developed to demonstrate a roundtrip efficiency in excess of 90%.

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A liquid alkali metal-BASE battery (ALL-BASE) is comprised of an alkali metal ion conducting BASE sandwiched between a liquid alkali metal as the anode and a metal salt as the cathode. At elevated temperatures during discharge, the alkali metal is oxidized at the anode forming metal ions, which migrate through the BASE and react with metal salt at the cathode. During charge, the above processes are reversed. In addition to the inherent advantage of the high roundtrip efficiency, the high-temperature ALL-BASE battery proposed can be thermally integrated with intermediate temperature SOFC (IT-SOFC) stacks, forming an economical, compact, lightweight hybrid system with very high system efficiency.

Approach

This project is directed toward the development of a high temperature (400~650°C) secondary storage battery based on ALL-BASE technology. Two types of high temperature batteries, sodium-based and potassium-based, will be developed.

The first type of battery, a sodium-based ALL-BASE, is based along similar lines to the one used in the ZEBRA batteries [1], but differs in three important aspects. They are: (a) The cathode uses salts which are not corrosive. Thus, inexpensive metallic materials can be used for the container, also facilitating the design and fabrication of compact, planar batteries. (b) Allows operation over a wider temperature range, making it possible to thermally integrate with a SOFC in a single thermal enclosure. (c) The batteries will be based on ultra-high strength, non-water sensitive, BASE [2-5]. This also allows for the fabrication of compact, planar cells, which can be readily integrated with a planar SOFC stack in a single thermal enclosure, as shown schematically in Figure 1.

The second type, which is a potassium-based ALL-BASE battery, is analogous to the sodium BASE battery, wherein the sodium ion is replaced by the potassium ion. Although the potassium BASE (K-BASE) has a lower ionic conductivity at 300°C than Na-BASE, the conductivity is still orders of magnitude higher than a typical oxygen ion conductor, such as yttria-stabilized zirconia (YSZ) used in a SOFC. At temperatures above 400°C, K-BASE is still an excellent K-ion conductor. In addition to possessing the three important aspects listed for the first type of battery, the K-BASE has three other unique prospectives: (1) With typical chlorides as cathodes, a potassium anode exhibits higher open circuit voltage (OCV) than sodium. For example, with a Na anode and Na-BASE, and $CuCl_2$ as the cathode, the OCV at 800 K (527°C) is 2.857 V, while with a K anode and K-BASE, the OCV is 3.19 V. (2) The density of potassium is 0.86 g/ml vs. 0.98 g/ml for sodium. Thus, it offers an advantage from the standpoint of weight and specific energy. (3) MSRI's patented process allows for easy fabrication of K-BASE, which is not feasible using the conventional process [2-5].

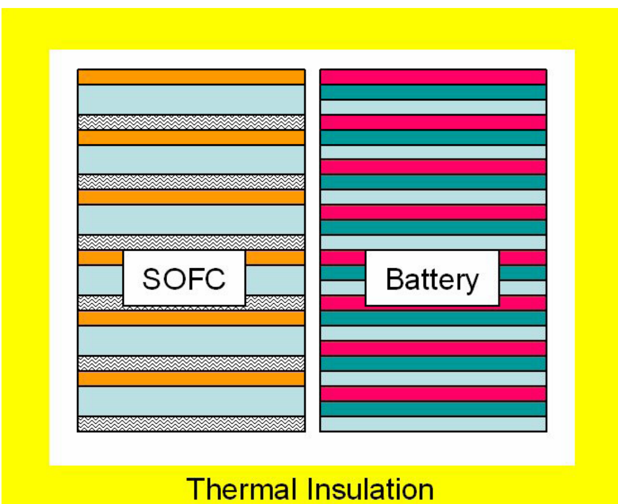

FIGURE 1. Proposed Thermally Integrated SOFC and Secondary Storage Battery System

Results

This project has barely started, and the accomplishments up-to-date are briefly described in what follows.

Identification of Suitable Electrochemical Couples

Identification of suitable electrochemical couples for the ALL-BASE battery is being performed. The prospective electrochemical couples should be sufficiently energetic, lightweight, not corrosive, not too volatile, and capable of forming a stable, porous metal structure in the cathode upon discharge. Since the anode is either liquid sodium or liquid potassium, the possible candidates for the cathode can be several metal salts. The metals, whose salts are used in the cathode, should be considerably more noble than sodium or potassium. This ensures a large enough free energy change upon discharge. The maximum amount of electrical energy that can be derived is $|\Delta G^o|$ (with $\Delta G^o < 0$), where the ΔG^o is the free energy of the reaction between sodium (or potassium) and the salt to form sodium (or potassium) salt and metal. The corresponding OCV is thus given by $E = -\Delta G^o/(nF)$, where n is the number of electrons participating the overall reaction and F is the Faraday constant (96,487 C/mol.). Table 1 lists the preliminary OCV calculations for a few potential candidate salts for the cathode.

As shown in Table 1, from the several possibilities for the electrochemical couples, the preferred ones (from the standpoint of specific energy) are the $CuCl_2$/Na and $CuCl_2$/K couples, with OCVs of 2.857 V for Na and 3.19 V for K, respectively. The AgF/Na and AgF/K

TABLE 1. A Material List of Possible High Temperature Electrochemical Couples

Electrochemical couple Na/Salt or K/Salt	ΔG^o for the reaction in kJ/mol. at 800 K	Open circuit voltage (OCV) (V)	Specific energy for the couple at 90% discharge efficiency in Wh/mol.	Specific energy for the couple in Wh/kg at 90% efficiency	Molar mass of the couple in kg
Na/$CuCl_2$	-551.357	2.857	137.8	763	0.1804
K/$CuCl_2$	-615.665	3.19	153.9	724	0.2126
Na/AgCl	-250.897	2.508	62.72	377.1	0.1663
K/AgCl	-274.237	2.842	68.56	377.9	0.1814
Na/AgF	-332.682	3.447	83.17	554.8	0.1499
K/AgF	-327.639	3.396	81.91	493	0.1660

couples are attractive from the standpoint of high open circuit voltage (about 3.4 V). Another attractive possibility is the use of AgF_2 as the cathode. At this point, no data regarding free energy are available. However, it is known that AgF_2 is quite stable and melts at 690°C [6]. The use of AgF_2 affords the possibility of increasing the specific energy since two atoms of fluorine are tied up with one atom of silver. Thus, upon discharge, two molecules of NaF (or KF) are formed. In addition, there are other possibilities. However, relevant thermodynamic data are not readily available. A detailed survey of the available thermodynamic data of other prospective electrochemical couples is continually being conducted in this project. If electrochemical couples superior to those given in Table 1 are identified, preliminary experiments will be conducted using the identified couples.

Fabrication of Tubular Na-BASE by MSRI's Patented Vapor Phase Process

The conventional process for the fabrication of Na-BASE involves sintering compacts of calcined powder containing BASE (and other sodium aluminates including $NaAlO_2$) at elevated temperatures (~1,600°C) in enclosed MgO containers to suppress vapor phase loss of Na_2O [7]. The necessity of using containers increases cost. Also, as some $NaAlO_2$ always remains along the grain boundaries, BASE made by the conventional process is susceptible to moisture and CO_2 attack from the atmosphere. In addition, the fracture strength of BASE made by the conventional process is generally low – on the order of 200 MPa or less. Also, the conventional approach cannot be used to make K-BASE since it does not form by a high temperature reaction.

MSRI has developed a novel process based on the concept of coupled transport, which has many advantages over the state-of-the-art [2-5]. The novel process for the fabrication of BASE by the vapor phase method developed at MSRI is described in what follows, and is used to fabricate both Na-BASE and K-BASE samples.

BASE Fabrication Process

(1) A slurry of a powder mixture of α-Al_2O_3 and tetragonal zirconia (3 mol.% Y_2O_3 + ZrO_2) is made. (2) The slurry is cast to form a tape of the desired thickness (~200 to 300 microns). (3) The tape is cut into square pieces of the desired dimensions (7 cm x 7 cm), or circular in shape for circular cells. (4) The cut pieces are sintered in air at ~1,400°C. The actual temperature will depend on the quality of powders. It can be as low as ~1,350°C. This leads to the formation of a fully dense (>99% of theoretical density) two phase material containing α-Al_2O_3 + tetragonal zirconia polycrystal. (5) The sintered pieces are then placed in a ceramic crucible surrounded by BASE powder as the source of Na_2O (or K_2O). This packing powder is made by conventional calcination, but is reused numerous times, each time simply replenishing the Na_2O (or K_2O) content by adding Na_2CO_3 (or K_2CO_3). The crucible is then heated to ~1,400°C and maintained at 1,400°C for about 15 to 20 minutes. Thereafter, the furnace is turned off. Upon cooling, highly conductive, strong and moisture/CO_2-resistant BASE results, ready for use in battery applications.

FIGURE 2. Photograph of Several Na-BASE Tubes Made (about 15 cm in length) by MSRI's Patented Vapor Phase Process

Figure 2 shows a photograph of several BASE tubes made by the MSRI patented vapor phase process, which also readily allows for the fabrication of thin, flat BASE plates, not feasible by the conventional process due to the warpage associated with liquid phase sintering in the conventional process. Typical BASE tubes fabricated by the conventional process for use in Na-S batteries are well in excess of 1 to 1.5 mm in thickness leading to a high ohmic area specific resistance (ASR). In contrast, the BASE made by this novel, patented process exhibits excellent properties, unmatched by BASE made using conventional processes.

Conclusions and Future Directions

- Several Na-BASE tubes with thin wall thickness have been fabricated using MSRI's patented vapor phase process. The tubes made are moisture resistant.
- Several suitable materials for high temperature electrochemical couples have been identified. Those couples will be further evaluated by measuring the OCVs.
- K-BASE tubes and square samples will be fabricated applying the same process as for making Na-BASE.

- ALL-BASE batteries will be constructed and tested in a controlled environment at elevated temperatures from 400°C to 650°C. The discharge depth and voltage vs. current characteristics will be evaluated.

References

1. C.-H. Dustmann, "ZEBRA Batteries Set to Take on the World", Batteries International, July (1994).

2. A. V. Virkar, J-F. Jue, and K-Z. Fung, "Alkali Metal Beta and Beta" Alumina and Gallate Polycrystalline Ceramics and Fabrication by a Vapor Phase Process", U. S. Patent No. 6,117,807.

3. A. V. Virkar, J-F. Jue and K-Z. Fung, "Alkali-Metal Beta and Beta" Alumina and Gallate Polycrystalline Ceramics and Fabrication by a Vapor Phase Method", U. S. Patent No. 6,537,940, Date of Issue: March 25, 2003.

4. A. V. Virkar, T. J. Armstrong, N. Weber, K-Z. Fung and J-F. Jue, in "High Temperature Materials", edited by S. C. Singhal, PV 2002-5, The Electrochemical Society, Inc., Pennington, NJ (2002).

5. G-Y. Lin and A. V. Virkar, J. Am. Ceram. Soc., 84 [6] 1321-26 (2001).

6. "CRC Handbook of Chemistry and Physics", 58th Edition, CRC Press, Cleveland, OH (1977).

7. J. L. Sudworth and A.R. Tilley, "The Sodium Sulfur Battery", Chapman and Hall, London, England, (1985).